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Band Model for Bismuth-Antimony Alloys*

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A simple model is proposed which unites many data on alloys of bismuth containing small amounts of antimony. Contrary to the usual interpretation of these data, we propose a crossing of the conduction and valence bands at L at about 6 at.% antimony (i.e., the *direct* gap, which is responsible for the very small effective masses in bismuth, vanishes at this composition).

WHILE pure bismuth and antimony are semimetals (good conductors at $T=0°\mathrm{K}$), their alloys are semiconductors (insulators at $T=0°\mathrm{K}$) over a wide range of composition. These alloys have been the subject of much experimental investigation, especially in the range of low antimony concentration. This article will consider the atomic fraction of antimony, x, to range from 0 up to about 0.2.

The data of these alloys are usually interpreted in terms of the known band structure of bismuth[1–3] as indicated in Fig. 1. There are conduction band minima at 3 equivalent L points in the Brillouin zone, and a valence band maximum at T. (The notation is that of Ref. 3.) Because the valence and conduction bands overlap, there are always carriers in these bands and we have metallic behavior. When antimony is added, this overlap is reduced and disappears[4,5] altogether at $x\approx 0.06$. At larger values of x, there is a thermal gap and we have a semiconductor. (Metallic behavior returns[5] when $x>0.3$.)

The purpose of this article is to point out that the behavior of these alloys can be accounted for by assuming that the relative positions of these 3 levels are linear functions of x:

$$\begin{aligned} T_{45}^{-}-L_s&=E_0{}^0-\alpha x,\\ L_s-L_a&=E_g{}^0-\beta x,\end{aligned}\tag{1}$$

where[2]

$$\begin{aligned} E_0{}^0&=38.5\ \mathrm{meV},\\ E_g{}^0&=15.3\ \mathrm{meV}.\end{aligned}\tag{2}$$

The coefficients α and β are estimated below. (Note that the symbols L_s, L_a, and T_{45}^{-} denote both levels and their energies.)

In interpreting the data in the metallic region ($x<0.06$), one generally assumes that the direct energy gap E_g is the same as in pure bismuth[4] ($E_g{}^0$). There is evidence for this in magnetoreflection measurements[6] on an alloy with $x=0.114$. Hebel and Smith observe direct transitions in this alloy which are characterized by the same direct gap and effective masses as in pure bismuth. Yet at $x=0.15$ the thermal gap[7] is 24 ± 3 meV. It seems unlikely that L_s-L_a would remain at 15 meV as x varies from 0 to 0.114 and then jump to 24 meV at $x=0.15$. (As the valence and conductions have a similar structure,[7] the thermal gap is probably also the direct gap.)

An alternate possibility is that L_s and L_a cross and have just reversed positions at $x=0.114$. (Interchanging L_s and L_a would not affect most measurements as they are "mirror" bands, except possibly in the heavy-mass direction which is usually not studied experimentally.) The crossing would occur at $x\approx 0.114/2=0.057$. Then from Eqs. (1) and (2)

$$\beta\approx E_g{}^0/0.057=270\ \mathrm{meV}.\tag{3}$$

This is consistent with the thermal gap mentioned above, for at $x=0.15$, $L_a-L_s=25$ meV.

We complete the model by determining α to fit the de Haas–van Alphen (dHvA) areas. This gives

$$\alpha\approx 500\ \mathrm{meV}.\tag{4}$$

The model, Eqs. (1)–(4), should be valid for x at least as large as 0.15.

With these numbers, L_a and L_s cross before a thermal gap appears. Thus in the semiconducting region $L_a>L_s$ and the thermal gap is defined by

$$E_t=L_a-\max(L_s,T_{45}^{-}).\tag{5}$$

Then E_t appears at $x_{sc}=0.06$. Jain[4] finds $x_{sc}=0.05$ and Ellett *et al.*[5] find 0.07. E_t is shown in Fig. 2 and is in fair agreement with experimental data. The main discrepancy occurs at the lower values of x and this may be explained qualitatively as follows: The thermal gaps are determined from the temperature dependence of the resistivity, and these measurements cannot be readily extended below about 25°K because of impurity conduction[7,8] and size effects.[7] But at 25°K the T_{45}^{-} valence

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[1] A. L. Jain and S. H. Koenig, Phys. Rev. **127**, 442 (1962); A. A. Lopez and S. H. Koenig, Solid State Commun. **4**, 513 (1966); S. H. Koenig, A. A. Lopez, D. B. Smith, and J. L. Yarnell, Phys. Rev. Letters **20**, 48 (1968); S. Mase, J. Phys. Soc. Japan **13**, 434 (1958); **14**, 584 (1959); L. G. Ferreira, J. Phys. Chem. Solids **28**, 1891 (1967); **29**, 357 (1968).

[2] G. E. Smith, G. A. Baraff, and J. M. Rowell, Phys. Rev. **135**, A1118 (1964).

[3] S. Golin, Phys. Rev. **166**, 643 (1968).

[4] A. L. Jain, Phys. Rev. **114**, 1518 (1959).

[5] M. R. Ellett, R. B. Horst, L. R. Williams, and K. F. Cuff, J. Phys. Soc. Japan Suppl. **21**, 666 (1966).

[6] L. C. Hebel and G. E. Smith, Phys. Letters **10**, 273 (1964).

[7] D. M. Brown and S. J. Silverman, Phys. Rev. **136**, A290 (1964).

[8] M. Dugué, Phys. Status Solidi **11**, 149 (1965).

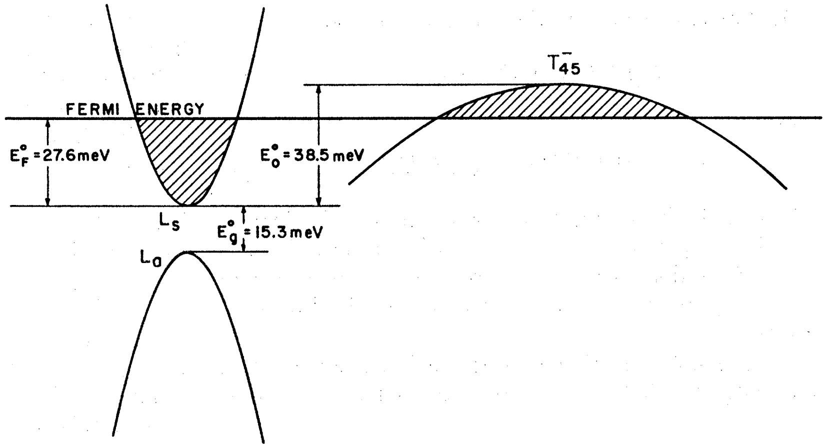

FIG. 1. Schematic band structure of pure bismuth at T and L near the Fermi energy. Crosshatching indicates electron (at L) and hole (at T) carriers.

band may be important even if it lies below L_s because it has a much larger effective mass, i.e., density of states. Thus at $x \approx 0.075$ the T_{45}^- band contributes about half of the electrons in the conduction band. The interpretation of the data becomes complicated but one can see that the effective thermal gap will be somewhat larger then given by Eq. (5) for the smaller values of x.

Further energy data come from tunneling measurements[9] on samples with $x=0.12$ and 0.135. In both samples the two highest-lying valence bands are 25 ± 5 and 40 meV below the bottom of the conduction band. The upper one is in approximate agreement with $E_t=17$ and 21 meV at $x=0.12$ and 0.135, respectively. At $x=0.12$, the T_{45}^- level lies 54 meV below the conduction band. If this is the level observed at 40 meV, the modification in the model required to fit it would be small and would not appreciably alter the agreement with the other data.

The electron Fermi surface in bismuth and in bismuth-antimony alloys ($x<0.06$) is highly anisotropic, but observers[5,10,11] find no change in this anisotropy as they increase the antimony concentration. Thus we may regard as scalars the ratios $m^c(x)/m^c(0)$ and $A(x)/A(0)$, where m^c and A are the *cyclotron* mass at the *Fermi energy* and the dHvA area, respectively.

To compare the model with the experimental values of these ratios, we make the following assumptions:

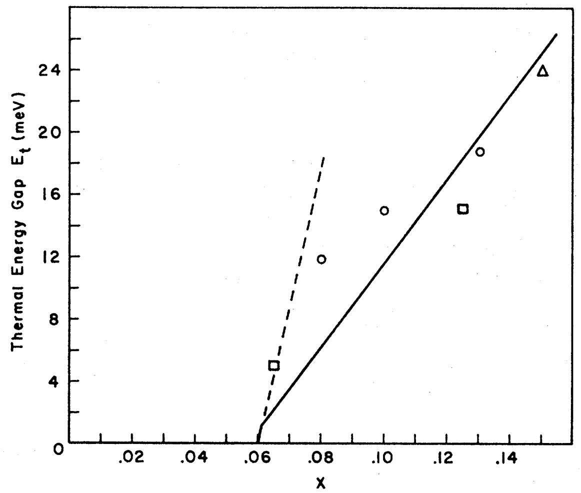

FIG. 2. Thermal energy gap. The solid curve follows from Eq. (5). The dashed line would be the thermal gap if the T_{45}^- valence band were dominant (see text). Circles, Ref. 8; triangles, Ref. 7; squares, N. B. Brandt and Ya. G. Ponomarev, Zh. Eksperim. i Teor. Fiz. **50**, 367 (1966) [English transl.: Soviet Phys.—JETP **23**, 244 (1966)].

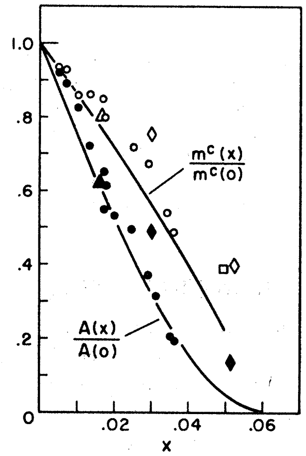

FIG. 3. The de Haas-van Alphen (dHvA) areas (closed symbols) and cyclotron masses (open symbols) versus composition relative to that for pure bismuth. The solid lines are the theoretical curves. Circles, Ref. 10; triangles, Ref. 11; diamonds, Ref. 5; square, Ref. 14. The masses of Kao *et al.* (Ref. 11) and Smith (Ref. 14) are from cyclotron resonance; the others are from the temperature dependence of the dHvA amplitude.

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[9] L. Esaki and P. J. Stiles, Phys. Rev. Letters **16**, 574 (1966).

[10] N. B. Brandt, L. G. Lyubutina, and N. A. Kryukova, Zh. Eksperim. i Teor. Fiz. **53**, 134 (1967) [English transl.: Soviet Phys.—JETP **26**, 93 (1968)]; N. B. Brandt and V. V. Shchekochikhina, Zh. Eksperim i. Teor. Fiz. **41**, 1412 (1961) [English transl.: Soviet Phys.—JETP **14**, 1008 (1962)].

[11] Yi-Han Kao, R. D. Brown, and R. L. Hartman, Phys. Rev. **136**, A858 (1964).

1. The electrons obey the Lax 2-band model[12]

$$E(1+E/E_g)=\sum_i \hbar^2k_i^2/2m_i \qquad (6)$$

and

$$m_0/m_i=1+2|M_i|^2/E_g \cong 2|M_i|^2/E_g\,, \qquad (7)$$

where M_i is the appropriate momentum matrix element and is independent[5] of x, and m_0 is the free-electron mass. Equations (6) and (7) are probably incorrect in the heavy-mass direction[13,3] and this may lead to small errors.

2. The hole effective masses are independent of x. (Actually the hole density of states effective mass is about 25% larger at $x=0.05$ than in pure bismuth.[14] This effect is unimportant for our purposes.)

To proceed we take the hole masses from Ref. 2 and from the electron masses given there we calculate the matrix elements M_i. Then from $E_g=|L_s-L_a|$ and $E_0=T_{45}^- - \max(L_s,L_a)$ we calculate the electron Fermi energy E_F by equating the number of electrons and holes. The dHvA area and the cyclotron mass ratios are then readily calculated. The latter is given by

$$m^c(x)/m^c(0)=(E_g+2E_F)/(E_g^0+2E_F^0)\,. \qquad (8)$$

These ratios are compared with experiment in Fig. 3; the agreement is good.

The crossing of L_s and L_a at $x\approx0.06$ is an essential part of this model. It should be easy to prove or disprove by magnetoreflection[6,12] measurements.

I wish to thank W. Goldburg for reading the manuscript.

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[12] R. N. Brown, J. G. Mavroides, and B. Lax, Phys. Rev. **129**, 2055 (1963); B. Lax, J. G. Mavroides, H. J. Zeiger, and R. J. Keys, Phys. Rev. Letters **5**, 241 (1960).

[13] M. H. Cohen, Phys. Rev. **121**, 387 (1961); J. O. Dimmock, MIT Laboratory Report No. 1, 1964, p. 41 (unpublished).

[14] G. E. Smith, Phys. Rev. Letters **9**, 487 (1962).

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Pseudopotential Calculation of the Thermal Expansion Coefficient of Sodium and Potassium*

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The total adiabatic potential is represented by a model based on electrostatic interactions among the ions and conduction electrons, Born-Mayer repulsion between the ions, a local pseudopotential interaction between ion cores and conduction electrons, and conduction-electron kinetic, exchange, and correlation energies. The three model parameters are determined for sodium and potassium by requiring agreement with the crystal binding energy and its first two volume derivatives at zero temperature and pressure. The phonon frequencies and Grüneisen parameters, the bulk-modulus pressure derivative, and the thermal expansion coefficient as a function of temperature are then calculated. These calculations are in good qualitative agreement with experimental results.

I. INTRODUCTION

THE aim of our present research program is to begin with the atomic description of crystals and calculate the thermodynamic properties. For nearly-free-electron metals it is convenient to describe the mechanical system of ions, electrons, and forces by means of pseudopotential perturbation theory. Thermodynamic functions may then be calculated by lattice dynamics theory.

Simple local pseudopotential models have been used to calculate the phonon spectrum of several metals,[1–7] and reasonably good agreement with experiment has been obtained. In the present paper we calculate the spectrum of Grüneisen parameters for sodium and potassium; this calculation may be compared with experiment in the form of the thermal expansion coefficient as a function of temperature. We have chosen to use Harrison's[1] modified point-ion pseudopotential, with two adjustable parameters, and we also include a Born-Mayer repulsion between ion cores, with one adjustable parameter.

Since we want our theory to be consistent with all the thermodynamic properties, the adjustable parameters are determined to obtain agreement with the measured crystal binding energy, lattice spacing, and compressibility at zero temperature and pressure. With

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[1] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

[2] L. J. Sham, Proc. Roy. Soc. (London) **A283**, 33 (1965).

[3] S. H. Vosko, R. Taylor, and G. H. Keech, Can. J. Phys. **43**, 1187 (1965).

[4] T. Schneider and E. Stoll, Physik Kondensierten Materie **5**, 331 (1966); **5**, 364 (1966).

[5] A. O. E. Animalu, F. Bonsignori, and V. Bortolani, Nuovo Cimento **64**, 159 (1966).

[6] N. W. Ashcroft, J. Phys. **C1**, 232 (1968).

[7] P. S. Ho, Phys. Rev. **169**, 523 (1968).